

WHAT IS CLAIMED IS:

1 1. A radiation-curable polyurethane produced by the process which comprises:
2 a) reacting at least one diisocyanate monomer with at least one polyol to provide
3 a polyurethane prepolymer containing unreacted diisocyanate monomer;
4 b) removing unreacted diisocyanate monomer from the polyurethane prepolymer
5 to provide polyurethane prepolymer of reduced unreacted diisocyanate monomer content,
6 and;
7 c) reacting the polyurethane prepolymer of reduced unreacted diisocyanate
8 monomer content with an acrylic monomer to provide radiation-curable polyurethane.

1 2. The radiation-curable polyurethane of Claim 1 wherein the diisocyanate
2 monomer is at least one diisocyanate monomer selected from the group consisting of 2,4- and
3 2,6-toluene diisocyanate, 4,4'-diphenyl methane diisocyanate, p-phenylene diisocyanate,
4 tolidene diisocyanate, hexamethylene diisocyanate, tetramethylxylylene diisocyanate,
5 isophorone diisocyanate and dicyclohexylmethane diisocyanate.

1 3. The radiation-curable polyurethane of Claim 1 wherein the polyol is at least
2 one polyol selected from the group consisting of polyether, polyester, polycarbonate,
3 polycaprolactone and hydrocarbon polyols having a number average molecular weight of
4 from about 100 to about 12,000.

1 4. The radiation-curable polyurethane of Claim 3 wherein the polyether polyol is
2 represented by the general formula $\text{HO}(\text{RO})_n\text{H}$, wherein R is an alkylene radical and n is an

3 integer large enough that the polyether polyol has a number average molecular weight of at
4 least about 250.

1 5. The radiation-curable polyurethane of Claim 4 wherein the polyether polyol is
2 a polytetramethylene ether glycol.

1 6. The radiation-curable polyurethane of Claim 3 wherein the polyol is a
2 combination of a high molecular weight polyol and a low molecular weight polyol.

1 7. The radiation-curable polyurethane of Claim 6 wherein the low molecular
2 weight polyol is an aliphatic polyol selected from the group consisting of ethylene glycol,
3 diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene
4 glycol, tripropylene glycol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, and the like.

1 8. The radiation-curable polyurethane of Claim 6 wherein the low molecular
2 weight polyol is less than about 20% of the combination of high molecular weight polyol and
3 low molecular weight polyol.

1 9. The radiation-curable polyurethane of Claim 8 wherein the low molecular
2 weight polyol is up to about 15% of the combination of high molecular weight polyol and
3 low molecular weight polyol.

1 10. The radiation-curable polyurethane of Claim 3 wherein the polyol is a
2 polyester of butanediol, hexanediol and adipic acid.

1 11. The radiation-curable polyurethane of Claim 1 wherein the polyurethane
2 prepolymer is of the general structure ABA wherein A denotes diisocyanate and B denotes a
3 polyol.

1 12. The radiation-curable polyurethane of Claim 1 wherein the removal of
2 unreacted diisocyanate monomer from the polyurethane prepolymer is accomplished through
3 a process of distillation.

1 13. The radiation-curable polyurethane of Claim 12 wherein the process of
2 distillation is accomplished through an agitated film distillation system.

1 14. The radiation-curable polyurethane of Claim 13 wherein the agitated film
2 distillation system comprises continuous units with internal condensers that can be combined
3 in series.

1 15. The radiation-curable polyurethane of Claim 12 wherein the process of
2 distillation utilizes a wiped film vacuum distillation process.

1 16. The radiation-curable polyurethane of Claim 1 wherein the removal of
2 unreacted diisocyanate monomer from the polyurethane prepolymer reduces the content of
3 unreacted diisocyanate monomer polyurethane prepolymer to less than about 2% by weight.

1 17. The radiation-curable polyurethane of Claim 16 wherein the removal of
2 unreacted diisocyanate monomer from the polyurethane prepolymer reduces the content of
3 unreacted diisocyanate monomer polyurethane prepolymer to less than about 0.5% by weight.

1 18. The radiation-curable polyurethane of Claim 1 wherein the removal of
2 unreacted diisocyanate monomer from the polyurethane prepolymer reduces the content of
3 unreacted diisocyanate monomer polyurethane prepolymer to less than about 0.1% by weight.

1 19. The radiation-curable polyurethane of Claim 1 wherein the acrylic monomer
2 possesses at least one reactive functionality.

1 20. The radiation-curable polyurethane of Claim 19 wherein the acrylic monomer
2 possessing at least one reactive functionality is selected from the group consisting of vinyl
3 carboxylic acid, acrylic acid, methacrylic acid, aminoalkyl acrylates, aminoalkyl
4 methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates and mixtures thereof.

1 21. The radiation-curable polyurethane of Claim 20 wherein the hydroxyalkyl
2 acrylate is selected from the group consisting of hydroxyethyl acrylate, hydroxyethyl
3 methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutylacrylate
4 and mixtures thereof.

1 22. The radiation-curable composition of Claim 1 wherein the polyurethane
2 prepolymer of reduced unreacted diisocyanate monomer content is end-capped with an
3 acrylate.

1 23. The radiation-curable polyurethane of Claim 1 wherein the reaction of at least
2 one diisocyanate monomer with at least one polyol provides for a molar excess of
3 diisocyanate monomer over polyol.

1 24. The radiation-curable polyurethane of Claim 23 wherein the molar excess of
2 diisocyanate monomer over polyol is from about 2:1 to about 30:1 molar ratio.

1 25. The radiation-curable polyurethane of Claim 24 wherein the molar excess of
2 diisocyanate monomer over polyol is from about 3:1 to about 20:1 molar ratio.

1 26. The radiation-curable polyurethane of Claim 25 wherein the reaction of at
2 least one diisocyanate monomer with at least one polyol has a solvent added thereto.

1 27. The radiation-curable polyurethane of Claim 26 wherein the solvent is
2 selected from the group consisting of dimethyl adipate and dimethyl phthalate.

1 28. The radiation-curable polyurethane of Claim 1 formed from a prepolymer of
2 step (b) having a NCO content of at least about 70% of the theoretical NCO content.

1 29. The radiation-curable polyurethane of Claim 1 formed from a prepolymer of
2 step (b) having a NCO content of at least about 80% of the theoretical NCO content.

1 30. The radiation-curable polyurethane of Claim 20 wherein the hydroxyalkyl
2 acrylate has a ratio of available hydroxyl functionality to the available NCO content of the
3 polyurethane prepolymer of reduced unreacted diisocyanate monomer content of from about
4 0.9:1 to about 1.2:1.

1 31. The radiation-curable polyurethane of Claim 30 wherein the hydroxyalkyl
2 acrylate has a ratio of available hydroxyl functionality to the available NCO content of the
3 polyurethane prepolymer of reduced unreacted diisocyanate monomer content of from about
4 1.05:1 to about 1.10:1.

1 32. The radiation-curable polyurethane of Claim 1 wherein step (c) can have
2 added thereto one or more inhibitors of free radical reactions in an amount of from about
3 50 ppm to about 1% by weight.

1 33. The radiation-curable polyurethane of Claim 32 wherein the inhibitor of free
2 radical reactions is 4-methoxyphenol.

1 34. The radiation-curable polyurethane of Claim 1 wherein step (c) can have
2 added thereto one or more catalysts in an amount of up to about 3% by weight.

1 35. The radiation-curable polyurethane of Claim 1 wherein at the temperature of
2 about 50°C the viscosity is from about 500 to about 30,000 cps.

1 36. A radiation-curable polyurethane comprising:

2 a) a polyurethane prepolymer terminated with a diisocyanate monomer selected
3 from the group consisting of 2,4- and 2,6-toluene diisocyanate, 4,4'-diphenyl methane
4 diisocyanate, p-phenylene diisocyanate, tolidene diisocyanate, hexamethylene diisocyanate,
5 tetramethylxylylene diisocyanate, isophorone diisocyanate, and dicyclohexylmethane
6 diisocyanate, said polyurethane prepolymer being the reaction product of one or more of the
7 said diisocyanate monomers and at least one polyol selected from the group consisting of
8 polyether, polyester, polycarbonate, polycaprolactone and hydrocarbon polyols having a
9 number average molecular weight of from about 250 to about 12,000 from which unreacted
10 diisocyanate monomer has been removed; said polyurethane prepolymer comprising no more
11 than about 2 wt % free diisocyanate monomer and having at least about 80% of theoretical
12 NCO content for pure ABA structure and;

13 b) an acrylic monomer possessing at least one reactive functionality selected
14 from the group consisting of vinyl carboxylic acids, acrylic acid, methacrylic acid,
15 aminoalkyl acrylates, aminoalkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl
16 methacrylates and mixtures thereof, said radiation-curable polyurethane containing a ratio of
17 available hydroxy functionality of the hydroxyalkyl acrylate to NCO content of the
18 prepolymer of reduced unreacted diisocyanate monomer content of from about 0.9:1 to about
19 1.2:1.

1 37. A substrate coated with a radiation curable polyurethane produced by the
2 process which comprises:

3 a) reacting at least one diisocyanate monomer with at least one polyol to provide
4 a polyurethane prepolymer containing unreacted diisocyanate monomer;

5 b) removing unreacted diisocyanate monomer from the polyurethane prepolymer

6 to provide polyurethane prepolymer of reduced unreacted diisocyanate monomer content,

7 and;

8 c) reacting the polyurethane prepolymer of reduced unreacted diisocyanate

9 monomer content with an acrylic monomer to provide radiation-curable polyurethane.